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RAPID SCREENING TECHNIQUE FOR HT MUSTARD BREAKDOWN PRODUCTS IN AQUEOUS MATRICES USING ION-EXCLUSION CHROMATOGRAPHY WITH UV DETECTION

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14. ABSTRACT

Methodology is described for rapidly screening aqueous matrices for major hydrolytic breakdown products of HT Mustard Mixture{H-bis(2-chloroethyl)sulfide; T-bis[2-(2-chloroethylthio)ethyl]ether}. Separations were carried out on an ion-exclusion column using acetonitrile/10 mN H2SO4 (1:10) as the mobile phase with quantitation by ultraviolet detection at 210 nm. Compounds detected and analyzed included bis(2-hydroxyethyl)sulfide, bis[(2-hydroxyethylthio)ethyl]ether ("T-alcohol"), and bis(2-hydroxyethylthio)ethane ("Q-alcohol"). Detection limits for all analytes were around 1 µg/mL.

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Thiodyglyco	Q-alcohol	Ion-exclusion Chromatography
T-alcohol	HT Mustard	Thiodyglycol sulfoxide

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PREFACE

The work described in this report was authorized under Project No. 778117, Assembled Chemical Weapons Assessment Program. This work was started in October 1998 and completed in September 1999. The experimental data are recorded in laboratory notebook 96-0055.

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FIGURE

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RAPID SCREENING TECHNIQUE FOR HT MUSTARD BREAKDOWN PRODUCTS IN AQUEOUS MATRICES USING ION-EXCLUSION CHROMATOGRAPHY WITH UV DETECTION

1. INTRODUCTION

Ion-exclusion chromatography with ultraviolet detection has been the Center's method of choice for screening aqueous environmental and demilitarization samples for bis(2-hydroxyethyl)sulfide(TDG), the major hydrolytic breakdown product of mustard (H)[bis(2-chloroethyl)-sulfide.* Mechanism of analyte retention and separation includes not only hydrophobic (reverse phase) interaction but also electrostatic interaction (Donnan exclusion) and size exclusion. Unlike the C-18 reverse phase columns previously used for this analysis, ion-exclusion columns were found to resist fouling even after repeated injections of decon samples.

The Center was tasked to upgrade this methodology to include the addition of the major hydrolytic breakdown products of HT mustard mixture {60% H; 40% T-bis[2-(2-chloroethylthio)ethyl]ether}.

$S(CH_2CH_2OH)_2$	$S(CH_2CH_2Cl)_2$	$O(CH_2CH_2SCH_2CH_2Cl)_2$
TDG	**H**	**T**

Methodology is described here to detect and quantitate HT breakdown products TDG, bis(2-hydroxyethyl)sulfoxide(TDGO), bis[(2-hydroxyethylthio)ethyl] ether("T-alcohol"), bis(2-hydroxyethylthio)ethane("Q-alcohol"), 1,4-thioxane, and 1,4-dithiane at trace levels in aqueous matrices.** The HT breakdown products are separated on an ion-exclusion column and upon elution, are detected and quantitated using ultraviolet (UV) detection. The feasibility of this method for the analysis of demilitarization samples is demonstrated.

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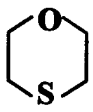
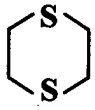
* Bossle, P.C.; Ellzy, M.W. *Detection of Thiodiglycol and Its Sulfoxide and Sulfone Analogues in Environmental Waters by High Performance Liquid Chromatography;* ERDEC-TR-035; U.S. Army Edgewood Research, Development and Engineering Center: Aberdeen Proving Ground, MD, 1993; UNCLASSIFIED Report (AD-A266 971).

** Bossle, P.C.; Ellzy, M.W. Rapid Screening Technique for HT Mustard Breakdown Products in Aqueous Matrices Using Ion-Exclusion Chromatography with UV Detection. Presented at the International Ion Chromatography Symposium, Baltimore, MD, 2002; Poster Presentation No. 80.

SO(CH2CH2OH)2 O(CH2CH2SCH2CH2OH)2 (CH2SCH2CH2OH)2

TDGO T-ALCOHOL Q-ALCOHOL





1,4-THIOXANE 1,4-DITHIANE

2. MATERIAL AND METHODS

2.1 Chemicals.

Water used in this study was distilled and deionized (18 meq/cm) using a Barnstead Megapure Model MP-6A System (Barnstead, Dubuque, IA). Analytical grade sulfuric acid was obtained from Mallinckrodt Chemical Works (St. Louise, MO). The HPLC grade acetontrile was purchased from Spectrum Laboratory Products, Incorporated (Gardenia, CA); TDG, 1,4-thioxane, and 1,4-dithiane were obtained from Aldrich Chemical Company (Milwaukee, WI); and TDGO was obtained from Chemical Services, Incorporated (West Chester, PA). The T- and Q- alcohol were prepared in-house and gave spectral data consistent with their chemical structure.

2.2 Instrumentation.

The chromatographic analysis was carried out using a Waters Millennium 2010 Data Work Station equipped with a Rheodyne Injector, a Waters Model 510 Pump, and a Waters Model 490 UV Detector (Waters Corporation, Milford, MA).

2.3 Chromatographic Procedures.

Ion-exclusion separations were performed using the following chromatographic parameters: column, Dionex IonPac ICE-AS1; temperature, ambient; eluent, 10 mN sulfuric acid/10 % acetonitrile, flow rate 1.5 mL/min; injection volume, 20 µL; and detection, UV (210 nm, 1.00 AUFS).

Stock solutions of each analyte were injected onto the column and the retention time for each analyte was determined. Calibration curves were obtained by injecting a known concentration (100, 50, 10, 5, 1, and 0.5 µg/mL) of each of the six analytes in deionized water into the chromatograph in triplicate and measuring the UV response obtained.

3. DISCUSSION AND RESULTS

Retention and separation of HT mustard breakdown products on an ion-exclusion column is by a mixed Donnan-exclusion, hydrogen bonding, and reverse phase mode mechanism. These non-ionic molecules are retained by passing the charged Donnan shield and adsorbing on the column. Charged organic and inorganic species, common in real world matrices, are repelled by the shield and are eluted in the void. The six analytes, containing thioether or sulfoxide moieties, have electron absorption bands in the 195-215 nm region and can be detected upon elution at 210 nm. For example, TDGO and TDG have relatively strong molar absorptivities of 1415 and 1271, respectively, at 210 nm.

A standard mixture of the six analytes in water, each at a concentration of 20 μg/mL, is shown in Chromatogram A (see the Figure). The peaks for the analytes are base line resolved for a 20-min run time with minimum quantifiable detection limits for all six species being approximately 1 μg/mL (S/N=3). Response to UV detection was linear (correlation coefficient >0.99) for all analytes over an injection range of 1-1000 μg/mL. Feasibility of this method was demonstrated with a real world HT mustard breakdown mixture as shown in Chromatogram B (see the Figure). With no sample preparation except filtration before injection, the resulting chromatogram shows analyte peaks free of matrix interferences.

4. CONCLUSION

Ion-exclusion chromatography with ultraviolet detection provides a rapid and direct screen for detecting and quantitating major HT mustard hydrolytic breakdown products (see Figure) in aqueous solutions at concentrations as low as 1 μg/mL. The feasibility of this new method is demonstrated with an analysis of an authentic HT mustard demilitarization sample.

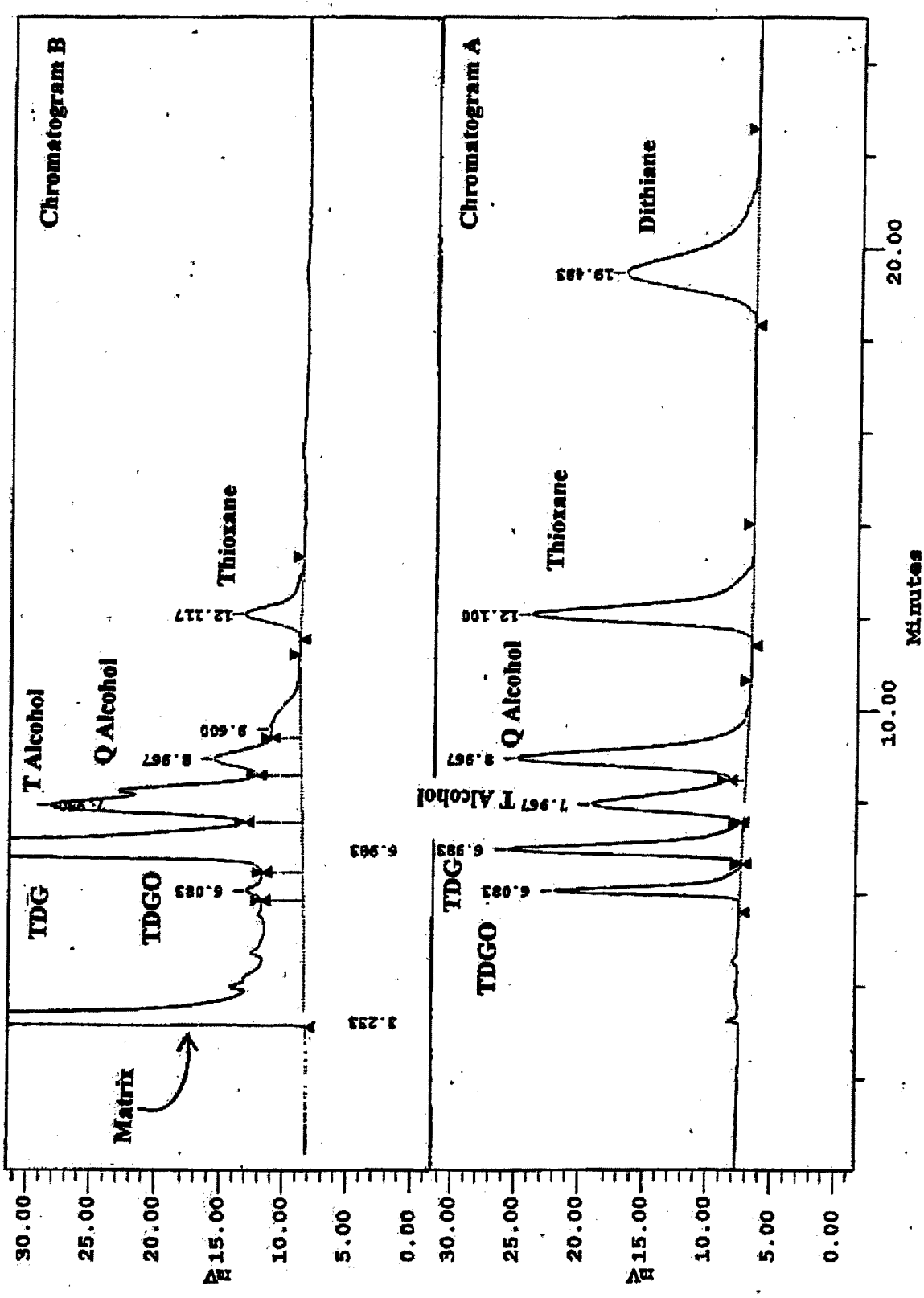


Figure. Ion-Exclusion Separation-UV Detection Chromatograms of (A) Standards at 20 µg/mL Concentration and (B) Neat Real World HT Mustard Breakdown Mixture.